

Replacement Solvents for Nonvolatile Residue (NVR) Removal from Painted Space Hardware

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1. Introduction

Paint strippers are complex formulations that comprise solvents, activators, corrosion inhibitors, thickeners, and evaporation retarders. Historically, the most effective (and most widely used) commercial products contain 60% to 70% methylene chloride, a chemical identified in the Clean Air Act (Act, section 112) list of Hazardous Air Pollutants (HAPs).

In 1994, an estimated 144 million pounds of methylene chloride was used for paint stripping applications in the United States.¹ On June 6 of that year, the United States Environmental Protection Agency (EPA) proposed National Emission Standards of Hazardous Air Pollutants (NESHAP) for aerospace manufacturing and rework facilities. The following year, the proposed standards were approved and promulgated in the Federal Register, Volume 60-September 1, 1995, under 40 CFR Parts 9 and 63 (National Emission Standards for Aerospace Manufacturing and Rework Facilities). These standards, and subsequent CFR updates (1996 and 1998), have required drastic reductions in the use of methylene chloride-based paint strippers for aircraft depainting operations.

Arnold and Uht have successfully employed the use of Hansen solubility parameters to identify methylene chloride replacements for organic contaminant (nonvolatile residue-NVR) removal from space hardware.² The simplicity of this approach led us to examine the feasibility of using a parameterized approach to identify methylene chloride replacement solvents for aircraft paint stripping applications.³ During our examination, it became apparent that the ability to predict the solubility behavior of paints would be of significant value when NVR sampling and cleaning of painted space hardware was necessary. We point out that paints are multi-component systems composed of inorganic compounds (pigments) and various classes of organic compounds (binders/resins, additives). NVR, on the other hand, generally comprises "like type" organic species.

In this report, we present our findings from a preliminary laboratory effort that was initiated to assess the feasibility of using solvent parameters as a predictive tool for NVR removal from painted/coated space hardware. Hansen's parameterized approach, used to predict the solubility behavior of single-component systems, is reviewed in Section 2. Our laboratory effort is described in Sections 3 and 4. The difficulties encountered when applying Hansen's parameterized approach to multi-component paint systems are discussed in Section 5.

2. Solubility Parameters

Hansen parameters can be used to predict the solubility behavior of organic liquids and polymers.^{4,5} The total Hansen parameter, δ_t , is given by:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \quad (1)$$

where each parameter describes a particular solubility property:

δ_t^2 = total Hansen parameter, equivalent to the Hildebrand parameter

δ_d^2 = dispersion component

δ_p^2 = polar component

δ_h^2 = hydrogen bonding component

In Hansen's three-dimensional model, an approximate spherical volume of solubility can be plotted for a given solute (Figure 1). The component parameters ($\delta_d, \delta_p, \delta_h$) define the center of the solubility sphere, and R , which is determined empirically, defines the radius of interaction. In theory, a solvent will be effective if its component parameters are contained within the boundary of the solute solubility sphere. The distance, $i^j D$, between the solvent component parameter coordinates ($i^j \delta_d, i^j \delta_p, i^j \delta_h$) and the center of the solute solubility sphere ($i^j \delta_d, i^j \delta_p, i^j \delta_h$) is calculated using Eq (2).* If $i^j D$ is less than the solute radius of interaction, R , the solvent is expected to dissolve the solute.

$$i^j D = [4(i^j \delta_d - i^j \delta_d)^2 + (i^j \delta_p - i^j \delta_p)^2 + (i^j \delta_h - i^j \delta_h)^2]^{1/2} \quad (2)$$

* The prefactor 4 is included to provide an approximately spherical "volume of solubility." We acknowledge that there is disagreement in the literature about the validity of doubling the dispersion scale to create a spherical solubility volume. Despite the disagreement, it is important to recognize that the use/exclusion of the pre-factor is not important unless the difference between the dispersion components of the solute and solvent ($i^j \delta_d - i^j \delta_d$) is significantly large compared to differences of the remaining two parameters, δ_p, δ_h .

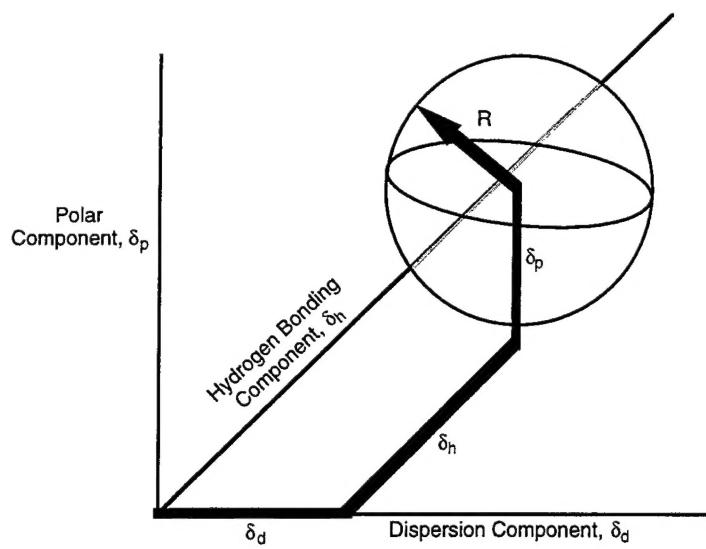


Figure 1. Representation of Hansen parameter solubility sphere with radius of interaction, R .

3. NVR Removal from Painted Surfaces

A method to collect and measure NVR from space hardware has been established.⁶ The procedure is similar to that described in ASTM E1235M-95 [Standard Test Method for Gravimetric Determination of Nonvolatile Residue (NVR) in Environmentally Controlled Areas] and ASTM E1560M-95 (Standard Test Method for Gravimetric Determination of Nonvolatile Residue from Cleanroom Wipers).⁷ In this method, a specified area (1 ft²) of the hardware surface is wiped with a clean cloth soaked with a 3/1 mixture (by volume) of 1,1,1-trichloroethane/ethanol. Next, the wiper is soaked and ultrasonically agitated with the same type of solvent mixture. The solvent is then filtered and concentrated in vacuo. The residual NVR is weighed.

Recently, ethyl acetate was proposed to replace the 1,1,1-trichloroethane/ethanol mixture since the Total Hansen Solubility Parameter, δ_t , of ethyl acetate ($\delta_t = 18.1$) is similar to that of 1,1,1-trichloroethane ($\delta_t = 17.7$).³ For most applications, this replacement can be justified. However, if painted surfaces are to be sampled, the potential for unfavorable interactions should be considered. For example, if the solvent dissolves one or more components of the paint, the dissolved component(s) could result in erroneously high NVR measurements. Unfavorable interactions might also include full removal of paint from the substrate, or a change in physical properties of the coating that is brought about when one or more components is selectively dissolved and removed from the bulk material.

For this reason, a preliminary laboratory effort was undertaken to assess the feasibility of using solubility parameters to predict the potential for the solvent to also dissolve paint when removing NVR from painted spacecraft surfaces. Coupons, painted with commercially available aerosol paints, were soaked in either 1,1,1-trichloroethane, ethyl acetate, or acetone. The coupons were visually monitored for changes in paint adhesion and/or coating degradation.

4. Experimental Details

Aluminum coupons (1 in. x 1 in.) were cleaned by sonicating in a 1/1 mixture of acetone/ethanol. Prior to cleaning, half the coupons were roughened with 360-A grit silicon carbide abrasive paper. This was done to assess surface morphology/paint adhesion effects. Each coupon was coated with either Krylon Interior/Exterior Aerosol Paint (Cherry Red) or Aervoe Aerosol Striping Paint (Traffic Blue). The paint was applied in a fume hood by spraying the coupons from a distance of approximately 12 in. A second coat was applied after 24 h. The final coating was dried at ambient temperature for approximately 90 h. Coupons were then soaked in 60 ml of solvent (acetone, ethyl acetate, or 1,1,1-trichloroethane) and visually monitored (Table 1).

The same "type" of solubility behavior was observed for all Aervoe Striping Paint coated coupons. In each case, the solvent penetrated the coating causing it to swell significantly. As the coating swelled, the adhesive bond was destroyed, and the paint lifted off the substrate. The rate at which the coating was removed was found to be dependent on substrate morphology. It took three, five, and ten minutes to completely remove the coating from the smooth substrates in acetone, ethyl acetate, and 1,1,1-trichloroethane, respectively (Figures 2 and 3). After 24 hours, the paint still adhered to the rough substrates, though the paint had blistered appreciably (Figure 4).

A different "type" of solubility behavior was observed for the Red Krylon Interior/Exterior Painted coupons. Rather than swelling and blistering, the paint dissolved. Surface morphology did not have a significant effect on the rate; however, the type of solvent did. Acetone and ethyl acetate dissolved the coating in minutes (Figure 5). 1,1,1-trichloroethane appeared to selectively dissolve only certain components of the coatings (Figure 6).

Table 1. Solvent Paint Interaction Summary

Paint/Coating	Acetone	Ethyl Acetate	1,1,1-Trichloroethane
Aervoe Striping	Blistered/ Swelled	Blistered/Swelled	Blistered/Swelled
smooth	3 min	5 min	10 min
rough	hours	hours	hours
Red Krylon	Dissolved in Minutes	Dissolved in Minutes	Dissolved Slowly (hours)

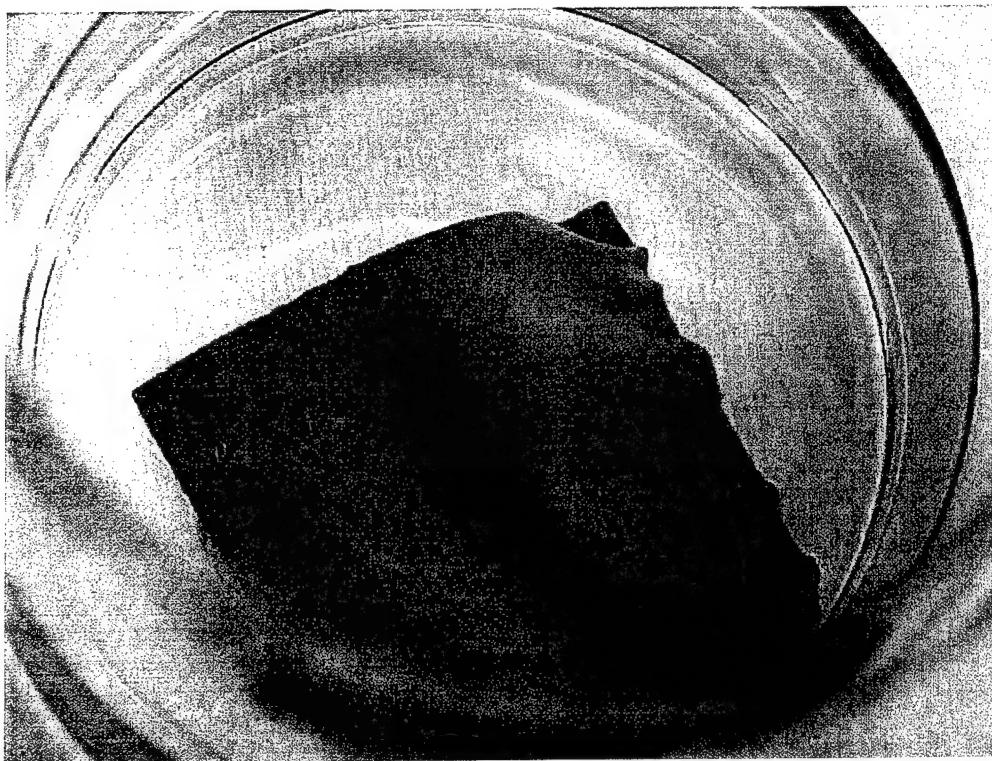


Figure 2. Aervoe Striping Paint in acetone (2 min).

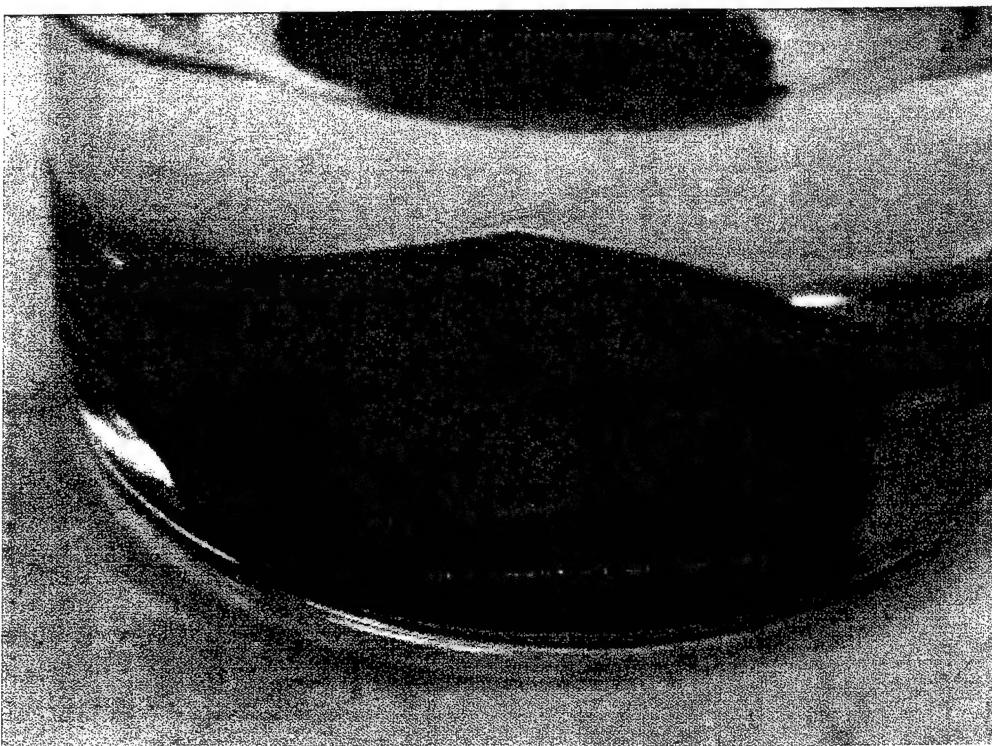


Figure 3. Aervoe Striping Paint in acetone (3 min).

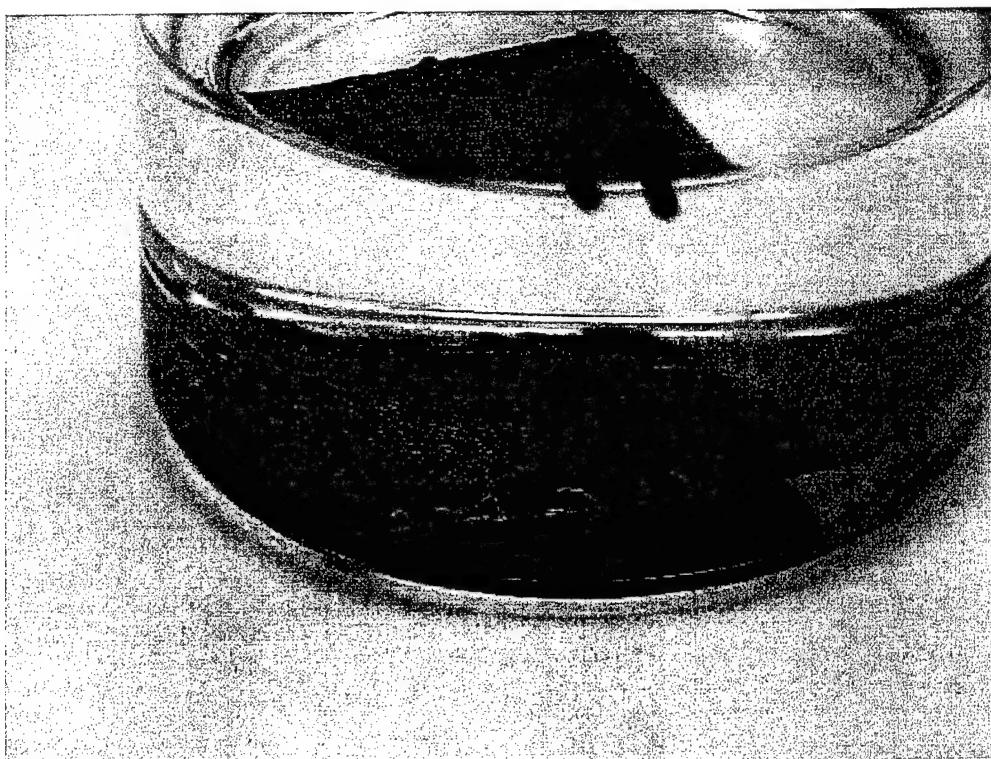


Figure 4. Aervoe Striping Paint in 1,1,1-trichloroethane (24 h).



Figure 5. Krylon Interior/Exterior Paint in ethyl acetate (3 min).



Figure 6. Krylon Interior/Exterior Paint in 1,1,1-trichloroethane (24 h).

5. Discussion

According to the manufacturer's product information, the base resin system for the Aervoe Striping Paint is a modified alkyd. The base resin system for the Red Krylon Interior/Exterior Paint is a mixture of polyester, acrylic polymer, and cellulose acetate butyrate. Hansen parameters for commercially available polymers that are representative of these classes of resins are tabulated in Table 2. For each solvent used, the distance (^{ij}D) between the solvent parameter coordinates ($^{i\delta_d}$, $^{i\delta_p}$, $^{i\delta_h}$) and the center of each polymer solubility sphere ($^{j\delta_d}$, $^{j\delta_p}$, $^{j\delta_h}$) was calculated and tabulated in Table 3. The empirically determined radius of interaction, R, for each polymer is listed in parentheses.⁴ Recall, if ^{ij}D is less than the solute radius of interaction, R, the solvent is expected to dissolve the solute.

Based on the information in Table 3, one would have expected 1,1,1-trichlorethane to be a good solvent for the Aervoe Striping Paint (a modified alkyd). Surprisingly, 1,1,1-trichlorethane was found to

Table 2. Hansen Parameters for Sample Base Resin Systems⁴

Polymer or Pigment (trade name, supplier)	δ_d (MPa $^{1/2}$)	δ_p (MPa $^{1/2}$)	δ_h (MPa $^{1/2}$)	R (MPa $^{1/2}$)
Alkyd, long oil (66% oil length, Plexal® P65 Polyplex)	20.4	3.4	4.6	13.7
Saturated Polyester (Desmophen® 850, Bayer)	21.5	14.9	12.3	16.8
Acrylic Poly(Methyl Methacrylate) (Rohm and Haas)	18.6	10.5	7.5	8.6
Acrylic Poly(Ethyl Methacrylate) (Lucite® 2042, Du Pont)	17.6	9.7	4.0	10.6

Table 3. Comparison of ^{ij}D (distance between solvent component parameter coordinates and center of solute solubility sphere) With Solute Radius of Interaction, (R).

Polymer or Pigment (trade name, supplier)	Ethyl Acetate ^{ij}D (R)	Acetone ^{ij}D (R)	Trichloroethane ^{ij}D (R)
Alkyd, long oil (66% oil length, Plexal® P65 Polyplex)	11.71 (13.7)	13.31 (13.7)	7.30 (13.7)
Saturated Polyester (Desmophen® 850, Bayer)	16.3 (16.8)	13.19 (16.8)	17.25 (16.8)
Acrylic Poly(Methyl Methacrylate) (Rohm and Haas)	8.88 (8.6)	6.28 (8.6)	8.82 (8.6)
Acrylic Poly(Ethyl Methacrylate) (Lucite® 2042, Du Pont)	8.45 (10.6)	5.64 (10.6)	5.85 (10.6)

be the least efficient. Likewise, the information in Table 3 suggests that the Krylon Interior/Exterior Paint, which contains polyester and an acrylic polymer, would exhibit very different solubility in ethyl acetate compared to acetone. This was not the case. Both solvents appeared to be equally efficient at fully dissolving the coating.

It is clear that Hansen's three-dimensional parameterized approach is not easily extended to multi-component systems such as paint. Frequently, polymeric resins/binders are modified. These modifications change the properties of the polymer and can result in very different solubility behavior. Unfortunately, detailed information about the binder/resin is often considered proprietary, and the only information that is typically provided by the manufacturer is the general polymer class. Moreover, solubility parameters are determined empirically and have been tabulated for only a limited number of polymers. This makes the extensive use of polymer solubility tables difficult. Finally, paints are complex formulations that comprise binder/resin, pigments, solvents, and additives. An example of a typical formulation for an Acrylic-Nitrocellulose paint (quantities given in parts per weight) is listed below.⁸

RBH White Titanium Dioxide Dispersion No. 6610	23.80
Diethyl Phthalate	5.40
1/2" RS Nitrocellulose (70% in ethyl alcohol)	5.90
Acryloid B-82 (50% solids in toluene)	28.64
Toluene	7.16
Methyl Ethyl Ketone	13.10
Methyl Isobutyl Ketone	16.00

After the solvents evaporate, the remaining binders/resins (organic polymers) and pigments (inorganic solids) comprise the largest weight fraction of the final coating. The diverse chemical natures of these organic and inorganic components suggest that they would exhibit very different solubility characteristics (Table 4). In fact, they do. Typical binders, such as cellulose, polyesters, and polyurethanes, show limited to moderate solubility in many organic liquids (Tables 5 and 6). Pigments, on the other hand, are far less soluble.

Table 4. Hansen Parameters of Resin/Binders (Polymer) and Pigments⁴

Polymer or Pigment (trade name, supplier)	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	R (MPa ^{1/2})
Cellulose Acetate Polymer (Cellidore [®] A, Bayer)	18.6	12.7	11.0	7.6
Cellulose Nitrate Polymer (1/2 sec; H-23, Hagedorn)	15.4	14.7	8.8	11.5
Saturated Polyester Polymer (Desmophen [®] 850, Bayer)	21.5	14.9	12.3	16.8
Permanengelb H 10 G Pigment (C.I. pigment yellow 81, Hoechst)	17.2	3.1	4.7	4.5
Phthalocyanine Blue Pigment (BG du Pont)	19.0	6.3	7.6	4.7
Monolite Fast Blue 3 RS Pigment (powder Cl vat blue, ICI)	22.1	13.3	17.4	14.3
Titanium Dioxide Pigment (Kronos RN 57, Titan)	24.1	14.9	19.4	17.2

Table 5. Comparison of $i_j D$ (distance between solvent component parameter coordinates and center of solute solubility sphere) With Solute Radius of Interaction, (R). If $i_j D$ is less than R, solvent is expected to dissolve the solute.

Polymer or Pigment (trade name, supplier)	Methylene Chloride $i_j D$ (R)	Benzene $i_j D$ (R)	Methanol $i_j D$ (R)
Cellulose Acetate Polymer (Cellidore® A, Bayer)	8.10 (7.6)	14.71 (7.6)	12.99 (7.6)
Cellulose Nitrate Polymer (1/2 sec; H-23, Hagedorn)	10.45 (11.5)	16.39 (11.5)	13.71 (11.5)
Saturated Polyester Polymer (Desmophen® 850, Bayer)	12.49 (16.8)	18.32 (16.8)	15.99 (16.8)
Permanengelb H 10 G Pigment (C.I. pigment yellow 81, Hoechst)	4.02 (4.5)	4.11 (4.5)	20.18 (4.5)
Phthalocyanine Blue Pigment (BG du Pont)	2.19 (4.7)	7.73 (4.7)	17.43 (4.7)
Monolite Fast Blue 3 RS Pigment (powder Cl vat blue, ICI)	15.41 (14.3)	20.98 (14.3)	14.3 (14.3)
Titanium Dioxide Pigment (Kronos RN 57, Titan)	34.4 (17.2)	24.95 (17.2)	17.83 (17.2)

Table 6. Comparison of $i_j D$ (distance between solvent component parameter coordinates and center of solute solubility sphere) With Solute Radius of Interaction, (R). If $i_j D$ is less than R, solvent is expected to dissolve the solute.

Polymer or Pigment (trade name, supplier)	Ethyl Acetate $i_j D$ (R)	Acetone $i_j D$ (R)	Hexane $i_j D$ (R)
Cellulose Acetate Polymer (Cellidore® A, Bayer)	10.34 (7.6)	7.22 (7.6)	18.52 (7.6)
Cellulose Nitrate Polymer (1/2 sec; H-23, Hagedorn)	9.43 (11.5)	3.03 (11.5)	17.19 (11.5)
Saturated Polyester Polymer (Desmophen® 850, Bayer)	16.3 (16.8)	3.19 (16.8)	23.63 (16.8)
Permanengelb H 10 G Pigment (C.I. pigment yellow 81, Hoechst)	6.54 (4.5)	10.01 (4.5)	7.53 (4.5)
Phthalocyanine Blue Pigment (BG du Pont)	8.02 (4.7)	9.09 (4.7)	13.09 (4.7)
Monolite Fast Blue 3 RS Pigment (powder Cl vat blue, ICI)	18.09 (14.3)	16.68 (14.3)	26.43 (14.3)
Titanium Dioxide Pigment (Kronos RN 57, Titan)	22.81 (17.2)	21.2 (17.2)	30.85 (17.2)

Pigment particles, on the order of 0.2–20 μm in size, possess “colloid-like” properties. Hence, the dispersion of particles is not thermodynamically favored unless there is favorable interaction with the liquid (favorable Gibbs free energy). Although Hansen parameters have been tabulated for some commercial pigments, their usefulness in predicting which solvents will promote “favorable” pigment/solvent interactions is complicated by the fact that the solvation of inorganic pigments involves donor-acceptor (Lewis acid-base) interactions, properties that are not adequately represented by Hansen parameters ($\delta_d, \delta_p, \delta_h$). Moreover, the surfaces of inorganic pigments are often coated with organic

resins or dyes (up to 40% resin/dye). Application of organic surface coatings yields new donor-acceptor complexes that can have significantly different solubility or swelling properties compared to the original pigment.

6. Conclusions

Hansen solubility parameters have been successfully employed as a predictive tool for dissolving single-component or “like-type” organic systems. A laboratory effort was initiated to determine whether this approach could be easily extended to multi-component systems. Specifically, we were interested in determining whether solubility parameters could be utilized to predict the solubility behavior of paints when NVR is removed from painted space hardware. Our examination revealed that although Hansen’s three-dimensional model can be a useful guide for systems with single or “like-type” components, it is not easily extended to multi-component paints. This is explained by the fact that the individual components of paint formulations exhibit very different solubility characteristics. In addition, solvent/pigment interactions are not adequately represented by Hansen parameters ($\delta_d, \delta_p, \delta_h$). Given that specific details about resins and pigments are rarely provided by the manufacturer, mixtures are not easily characterized. Finally, the ability to predict the solubility behavior of multi-component systems is further complicated by the fact that the properties of mixtures can be very different from those of the individual components.

In conclusion, caution should be used when utilizing solubility parameters as a predictive tool for applications in which NVR removal or cleaning is performed on painted space hardware. Clearly, it is not safe to assume that a particular solvent is safe for all paints in a class (e.g., nitrocellulose paints or alkyd paints), even if the solvent was found to be safe on one paint in that class. To mitigate risk associated with using solvents on painted surfaces, it is best to perform a quick test on a per case basis.